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ABSTRACT

Using ab initio (with effective core potentials) electronic structure theory, the equilibrium geometry and singlet-triplet separation was determined for CBr_2 . The triplet was computed using a single configuration SCF wavefunction, while the singlet state used a two configuration MCSCF wavefunction. This model is based on previous work on CH_2 and is discussed in detail. The Br effective core potentials are compared to all electron calculations for CHBr and found to give very similar results. The bond angle of the singlet is in agreement with experiment, while the computed triplet bond angle is very different from experiment. The singlet was computed to be ~ 8 kcal/mole lower than the triplet.

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Introduction

In a previous paper¹ we reported on the structure and energetics of several simple halogenated carbenes; CHF, CHCl, CHBr, CF₂ and CCl₂. At that time we noted that much work had been done on the reactions of CBr₂, but we were unable to investigate CBr₂ because of the size of the calculation. With the aid of effective core potentials, this problem is now tractable.

The structure of both the singlet and triplet have been determined using electron diffraction.³ The carbon-bromine bond distance was found to be 1.74 Å for both the singlet and triplet state. The singlet state was assigned a bond angle of $\sim 114^\circ$, while the triplet state was assigned an angle of $\sim 150^\circ$. CBr₂ has been assumed to be a ground state singlet based on the failure to observe nonsterospecificity in the addition reactions to olefins.⁴

Theoretical Approach

In this work we used the same theoretical approach as used previously¹ which is based on previous work^{5,6} on CH₂. The work on CH₂ suggests that reliable structures and a reasonable singlet-triplet separation can be obtained by treating the 3B_1 as a single determinant self-consistent field (SCF) wavefunction.

$$1a_1^2 \quad 2a_1^2 \quad 1b_2^2 \quad 3a_1 \quad 1b_1 \quad ; \quad ^3B_1, \quad (1)$$

while the 1A_1 state is treated with a two configuration MCSCF calculation,

$$\begin{array}{cccccc}
 c_1 & 1a_1^2 & 2a_1^1 & 1b_2^2 & 3a^2, & \\
 & & & & & 1A_1 \\
 + c_2 & 1a_1^2 & 2a_1^2 & 1b_2^2 & 1b_1^2 &
 \end{array} \quad (2)$$

Using this treatment, the near Hartree-Fock limit calculation of Meadows and Schaefer⁷ yields a separation of 10.9 kcal/mole. This is in excellent agreement with the accurate CI result of 10.6 kcal/mole obtained by Bauschlicher and Shavitt.⁶ Based on error analysis they concluded a singlet-triplet separation of ~ 9.0 kcal/mole which is in agreement with the determination of Lengel and Zare⁸ and the large number of chemical determinations.⁹⁻¹³ The previous work also showed good agreement between the limited experimental geometry information and our computed results.

The all electron basis sets use Dunning's double zeta (DZ) contractions. The hydrogen basis uses his (4s/2s) contraction¹⁴ of Huzinaga's primitive set¹⁵ (with a scale factor of 1.2); for carbon we used the (9s5p/4s2p) contraction¹⁴ of Huzinaga's primitive set¹⁵; for chlorine the (12s9p/6s4p) contraction¹⁶ of Veillard's primitive set¹⁷; and for bromine Dunning's (14s11p5d/8s6p2d) contraction of his own primitive set.¹⁸ (This basis set was tabulated in our previous paper¹). The valence electron basis sets and effective core potential parameters are taken from Kahn et al.¹⁹ The 3s and 3p Gaussian basis functions were not contracted, producing a valence basis (3s3p/3s3p) for Cl and bromine. Br used the 11 term fit to the effective core potentials, while Cl used a 9 term fit.

As we noted in our previous paper the addition of a d polarization functions to carbon was needed to obtain a reasonable singlet-triplet separation, while the addition of polarization functions to the substituents had little effect on the singlet-triplet separation. The DZ + d basis

starts from the DZ basis and adds a d function to the carbon. Based on the optimum carbon d functions we obtained previously, a d exponent of $\alpha = 0.4$ was used. We also noted that the C-Cl bond length in $\text{CHCl}^1\text{A}'$ was too long by 0.07\AA . We attributed this to the lack of d functions on Cl. In order to improve the bond lengths a DZ plus polarization (DZP) was also used. This basis set starts with the DZ basis and adds d functions to both C and Br. Both d exponents were $\alpha = 0.4$

Effective Core Potential Tests

In order to evaluate the use of effective core potentials (ECP) some tests were run comparing the valence electron with the all electron calculations. At the CCl_2 DZ computed geometries, the singlet-triplet separation of -2.00 kcal/mole compared to the -2.9 kcal/mole using the all electron DZ basis set. More extensive tests were run for CHBr and are summarized in Table I. The bond length and angles are in good agreement and the singlet-triplet separation is in error by a maximum of 2.3 kcal/mole. The carbon Mullikin populations computed using ECP's are in agreement with those computed in the all electron calculation. We should note that the difference between the singlet-triplet separation in CH_2 at the DZ + d level is 12.8 kcal/mole versus about 9 kcal/mole for the best estimates. The use of effective core potentials appears to introduce about an additional 2 kcal/mole error to this model.

Results and Discussion

The geometry was optimized for both the DZ and DZP basis. Using the optimum geometry computed with the DZ basis, the singlet-triplet separation was evaluated with the DZ + d basis. The results of these calculations are summarized in Table II and along with the previous work in Table III.

We compute the singlet to be 7.7 kcal/mole lower than the triplet at the DZ + d level and 8.6 kcal/mole lower with the DZP basis. This difference between the DZ + d and DZP is small and of about the same size as for CH₂ and CF₂. This small difference is additional support for our previous calculations which used only a DZ + d basis.

As noted above, this method treats the triplet better than the singlet by ~ 3 kcal/mole for CH₂, but the effective core potentials favor the singlet. Since these errors are of about the same magnitude and in opposite directions the singlet-triplet separation is probably very reasonable, but at this level of calculations not definitive.

Our previous explanation was based on the destabilization of the triplet by electron withdrawing substituents. As expected for the less electronegative Br, CBr₂ has a smaller singlet-triplet separation than CCl₂, however the substitution of Br for Cl in both CHCl and CCl₂ causes only a small change in the splitting. As with all our previous calculations, except CF₂, the total carbon Mulliken population is greater for the triplet, while the singlet has a larger carbon 2s population.

The bond lengths at the DZP level are shorter than the DZ, the singlet shortening by 0.08 Å. At the DZP level, the singlet and triplet bond lengths are very similar, but both are ~ .1 Å longer than the experimental³ result of 1.74 Å, which is 0.2 Å shorter than the C-Br experimental bond length in CH₃Br²⁰. For CH₃Br the computed²¹ bond length at the DZ-SCF level is 0.04 Å too long. If Cl is substituted for Br, the shortening going from CH₃Cl (1.781 Å)²⁰ to CHCl (1.689 Å)²² is 0.09 Å. The difference in bond length for CBr₂ is attributed to the limited basis set, the use of effective core potentials and any experimental uncertainty.

The single bond angle is in good agreement with experiment both being $\sim 112^\circ$. The triplet bond angles differ greatly, the computed value of 127° is 23° smaller than the experimental result of $\sim 150^\circ$. This difference is far larger than can reasonably be expected. One possible explanation for the large 3B_1 angle is a result of observing vibrationally excited CBr_2 . At the SCF level CBr_2 3B_1 has a barrier of $\sim 10,000\text{ cm}^{-1}$, for CH_2 the barrier was reduced by $\sim 30\%$ at the CI level.⁶ Therefore, the higher vibrational levels of CBr_2 would appear linear. The experiment obtains the geometry for the weighted average of all populated levels, so the formation of vibrationally excited CBr_2 molecules would make the bond angle appear larger. We should also note that the interpretation of the experiments is not always simple. In a previous study on $BrCCl_3$,²³ they had some uncertainty as to the molecules present and an incomplete explanation for the long C-Br bond. One explanation for the long C-Br bond length was the presence of excited states. While we are unable to completely resolve the difference between our calculations and experiments, we feel that our 3B_1 bond angle of 127° is more accurate than the $\sim 150^\circ$ of the experiment.

Conclusions

Calculations show CBr_2 to be a ground state, singlet in agreement with assumptions based on experimental data. The singlet bond angle is in agreement with electron diffraction studies, while the triplet bond angle is very different from experiment. One possible explanation for this difference is the presence of vibrationally excited 3B_1 CBr_2 .

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Table I. Comparison of all electron versus valence electron calculation for CHBr . The bond lengths are in \AA and the separations are in kcal/mole, with a positive sign indicating the triplet being lower.

	SINGLET		TRIPLET			
	All	Valence	All	Valence	All	Valence
	DZ					
RCH	1.103	1.105	1.075	1.075		
RCBr	1.972	1.961	1.891	1.888		
\ddagger	102.6	102.0	125.6	124.8		
separation					12.4	10.1
C2s population	1.83	1.85	1.48	1.50		
C2p population	2.30	2.28	2.71	2.75		
	DZ + d					
separation					1.1	0.1

Table II. Summary of CBr_2 calculations. Bond length is in \AA and total energy is in hartrees.

A negative sign for the singlet triplet separation (S-T) indicates the singlet is lower.

Molecule	Basis	S-T Separation in kcal/mole	Triplet			Singlet				
			R(CH)	R(CX)	θ	E	R(CH)	R(CX)	θ	E
CBr ₂	DZ	1.2		1.888	127.4	-64.52528		1.958	110.6	-64.52335
	DZ + d	-7.7		1.888	127.4	-64.55717		1.958	110.6	-64.56944
	DZP	-8.6		1.844	127.3	-64.57832		1.875	110.1	-64.59194
exp ^a				1.74 ~ 150				1.74 ~ 114		
2s population ^b				1.59				1.93		
2p population				2.64				2.15		
total population				6.22				6.08		

^areference 3

^bpopulations taken from DZ basis

Table III. Summary of computed equilibrium geometries and singlet-triplet separation. The bond lengths are in Å and the bond angle in degrees. The separations are in kcal/mole where a positive sign indicates the triplet is lower. All calculations except CHBr and CBr₂ represent optimizations at the DZ + d level. CHBr is optimized at the DZ level and CBr₂ at the DZP level.

	TRIPLET			SINGLET			
	R(CH)	R(CX)	θ	R(CH)	R(CX)	θ	Δ
CH ₂	1.075		128.8	1.106		102.5	12.8
CHBr	1.075	1.891	125.6	1.103	1.972	102.6	1.1
CHCl	1.075	1.735	123.3	1.101	1.762	102.0	-1.6
CHF	1.077	1.321	120.4	1.111	1.325	102.2	-9.2
CBr ₂		1.844	127.3		1.875	110.1	-7.7
CCl ₂		1.730	125.5		1.756	109.2	-13.5
CF ₂		1.311	117.8		1.305	104.3	-44.5